Glass and Ceramics Vol. 59, Nos. 9 – 10, 2002

RAW MATERIALS

UDC 666.1.022:66.011

KANAZITE: A PROMISING MATERIAL FOR GLASS MELTING

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Translated from Steklo i Keramika, No. 9, pp. 21 – 25, September, 2002.

A method for producing glass omitting the liquid phase, i.e., production of glass based on kanazite synthesized by hydrothermal treatment of amorphous rocks, is developed and scientifically substantiated. Kanazite is a complex glass material suitable for glass production without adding glass-forming components and clarifying or decolorizing agents. Owing to its amorphous phase composition and fine dispersion of components, kanazite is highly reactive.

The study of mineral resources and ways for their optimum use has great significance for the construction materials industry, including glass production.

Contemporary mineral materials available for the glass industry do not satisfy the demand of glass factories, which has a negative effect on economic parameters and the quality of the product [1].

The environmental safety of glass-melting processes has of late caused substantial concern in view of the use of crystalline quartz in the glass and ceramic industry. After the USA classified silicon dioxide used in the silicate industry as a carcinogenic of the fist group, many state agencies have started revising regulations for the permissible duration of the effect of materials containing crystalline quartz on people [2]. Consequently, replacement of carcinogenic quartz sand in the glass industry by amorphous rocks (perlite, diatomite, tripolite, etc.) can fundamentally solve this problem.

The characteristics specific for amorphous rocks include, on the one hand, the presence of active amorphous silicic acid, and on the other hand, a finely disperse structure, a small volume mass, and low thermal conductivity. The combination of these properties is responsible for the high absorption activity of such rocks and the possibility of using them as adsorbents, dryers, catalysts, filtering and heat-insulating materials, carriers, and fillers.

Russia has extensive deposits of different siliceous rocks: perlite, pumice, obsidian, opoka, diatomite, tripolite, spongolite, etc. [3]

The author together with V. V. Nasedkin (Doctor of Geology and Mineralogy, IGÉM Institute of the Russian Academy of Sciences) compiled a map of highly siliceous rocks of the Russian Federation, which was used in preparing the atlas “Natural resources and environment in the Russian Federation” (Moscow, NIA – Priroda, 2002).

The prospected reserves of these rocks alone exceed 1.6 billion tons. Russia occupies the leading place in the world in this respect. However, siliceous rocks are mainly used in the production of cement (as the hydraulic component), in construction, and heat-insulating industries. Diatomite, opoka, and tripolite are not yet used in state-of-the-art technologies (filtration, fillers, dryers, etc.). In particular, rocks and their waste as complex materials are used at some glass factories in Russia [4, 5]. Metallurgical slag, including blast furnace and ferrochromium slag and industrial waste such as waste catalysts, are successfully and extensively used in the production of tinted-glass bottles.

However, chemical heterogeneity of the majority of rocks and their high content of colorant oxides limit the possibilities of their application in glass melting. The known methods of treatment and homogenization of theses rocks do not yield sufficiently positive results. As a consequence, the topicality of developing methods enabling the use of local materials in the production of glass articles is obvious. Research and development studies of complex chemical processing of rocks containing SiO_2 in the amorphous form (perlite, diatomite, pumice, opoka, etc.) that was recently carried out at the “Stone and Silicates” research-and-production company (Erevan) offer a solution for the specified problem.

A technology has been developed for complex hydrothermal processing of silicon-bearing rocks into a number of silicate products (liquid glass and sodium metasilicate nanohydrate, amorphous silica, etc.) and into a complex glass material named kanazite, which exists in various chemical compositions (crystal glass, dark green container glass, sheet glass, light-engineering glass, etc.).

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Kanazite is a complex glass material constituting cemented aggregates of silicate compounds, which are suitable for glass melting without adding glass-forming compounds or clarifying and decolorizing agents. The material has high dispersion, homogeneity, and chemical purity. The composition of kanazite in the general form can be expressed by the following formula :

$$xR_2O \cdot yRO \cdot zR_2O_3 \cdot nSiO_2 \cdot mH_2O,$$

where x, y, z, n, and m are numerical coefficients.

The development of kanazite had the purpose of radically changing the existing method of glass batch preparation and to change over from dry mixing of solid components to mixing their solutions or suspensions. It was assumed that the hydrothermal-chemical method of preparing the glass batch should accelerate the reactions between its components and formation of silicates, since the glass-forming components in this case react in the form of solutions [6].

Kanazite synthesized on the basis of pure oxides and used for production of clear glass was named kanazite-1 and kanazite produced directly from rocks containing colorant impurities in great quantities is called kanazite-2 [7].

The main advantages of the hydrothermal batch (kanazite) are as follows.

Silica in the composition of kanazite exists either as an amorphous hydrated modification, or in the form of hydropolysilicate of bi- and trivalent metals (Ca, Mg, Pb, Al, etc.). The silica chemical bonds Si – O – Si in the structure of the obtained silicates are replaced by Si – O – Me and Si – O – OH bonds, which have more free energy and, accordingly, require less energy for their destruction. Thus, melting of kanazite with the composition of potassium-lead crystal glass takes place at temperatures lower by 200 – 400°C and proceeds faster by 2 – 3 h than the standard batch of the same composition.

This method of synthesis of kanazite based on mixing solutions or suspensions of glass-forming components that react with each other in the course of synthesis ensures its total homogeneity.

The content of colorant impurities in kanazite can be reduced to $10^{-3} – 10^{-4}$%, since the initial solutions (liquid glass, solutions of Ca, Mg, and Pb nitrates, etc.) are more susceptible to deep purification than solid materials. Contrary to the usual batch, the components of kanazite almost do not volatilize.

Alkali metal silicates, which are the main kanazite-forming components, have a great degree of purity, since most colorant pigments, as rule, remain in the precipitate after filtration (in alkaline alumosilicates). Furthermore, alkali silicate solutions obtained according to the developed technology can be subjected to deep purification by magnetic treatment, which makes it possible to synthesize kanazite with compositions of specials glass: optical, uviol, etc.

The main sources of silica for kanazite-1 that has the composition of clear glass are solution of alkaline silicates. However, the weight ratio of silica to alkalis in these compositions is at best equal to 3.8, which does not meet the required glass composition, in which the ratio $SiO_2 : R_2O$ varies from 4 to 5. The required ratio in kanazite can be provided in two ways:

– decreasing the content of the alkaline components in the mixture by filtration;

– increasing the quantity of silica in kanazite by adding it externally.

Synthesis of kanazite-1 with the composition of potassium-lead crystal glass. Hydrothermal treatment of perlite is implemented simultaneously with sodium and potassium alkali treatment; as a consequence, sodium and potassium liquid glass is produced. Next, high-modulus lead silicate is formed based on the reaction of the latter with lead nitrate solution and, after its separation from the mother solution by filtration, is mixed with potassium liquid glass for the purpose of raising its silicate modulus.

The production of kanazite-1 with the crystal glass composition containing 24% PbO is protected by the inventor's certificate (USSR Inventor's Certif. No. 496800). The approximate chemical composition of crystal kanazite is as follows (wt.%): 58.20 SiO_2, 24.88 PbO, 14.32 K_2O, 0.38 Na_2O, 0.83 ZnO, 1.00 B_2O_3, 0.018 Fe_2O_3, and 0.38 calcination loss.

Perlite is treated with caustic potassium solution for the purpose of producing potassium silicate that is introduced into the composition of kanazite for crystal glass production.

Perlite treated by caustic soda solution produces sodium silicate, which is the basis for the production of solution of high-modulus lead silicate $(PbO \cdot SiO_2) \cdot nSiO_2$, which introduces 37% of fixed SiO_2 into the kanazite solution and also 22% of the required amount of additional silica synthesized as the result of reaction between nitric acid and sodium silicate.

It can be seen in Fig. 1 that part of the milled perlite (grain size not more than 0.25 mm) is mixed with caustic potassium solution of the required concentration (converted to Na_2O it correlates with the concentration of 80.6 g/liter) under a ratio of the liquid phase to the solid phase of L : S = 1.2 : 1.0 and sent to autoclave treatment at 200°C for 60 min. As the result, potassium liquid glass $K_2O \cdot 2.3SiO_2$ is synthesized.

The remaining part of perlite is similarly mixed with caustic soda solution (concentration of Na_2O 80.6 g/liter with L : S = 1.2 : 1.0; treatment temperature 180°C, duration 60 min) for the synthesis of sodium liquid glass $Na_2O \cdot 3SiO_2$.

The resulting solutions of sodium and potassium liquid glasses are filtered on drum vacuum filters at a temperature of 80 – 90°C.

Potassium liquid glass enters into the synthesis of kanazite, and sodium liquid glass reacts with lead nitrate in the presence of nitric acid to produce high-modulus lead silicate according to the following reaction:

$$Na_2O \cdot nSiO_2 + Pb(NO_3)_2 = PbO \cdot nSiO_2 + 2NaNO_3.$$

Lead nitrate dissolves well in water (127.3 g is dissolved in 100 g of water at 100°C), and as the lead nitrate solution

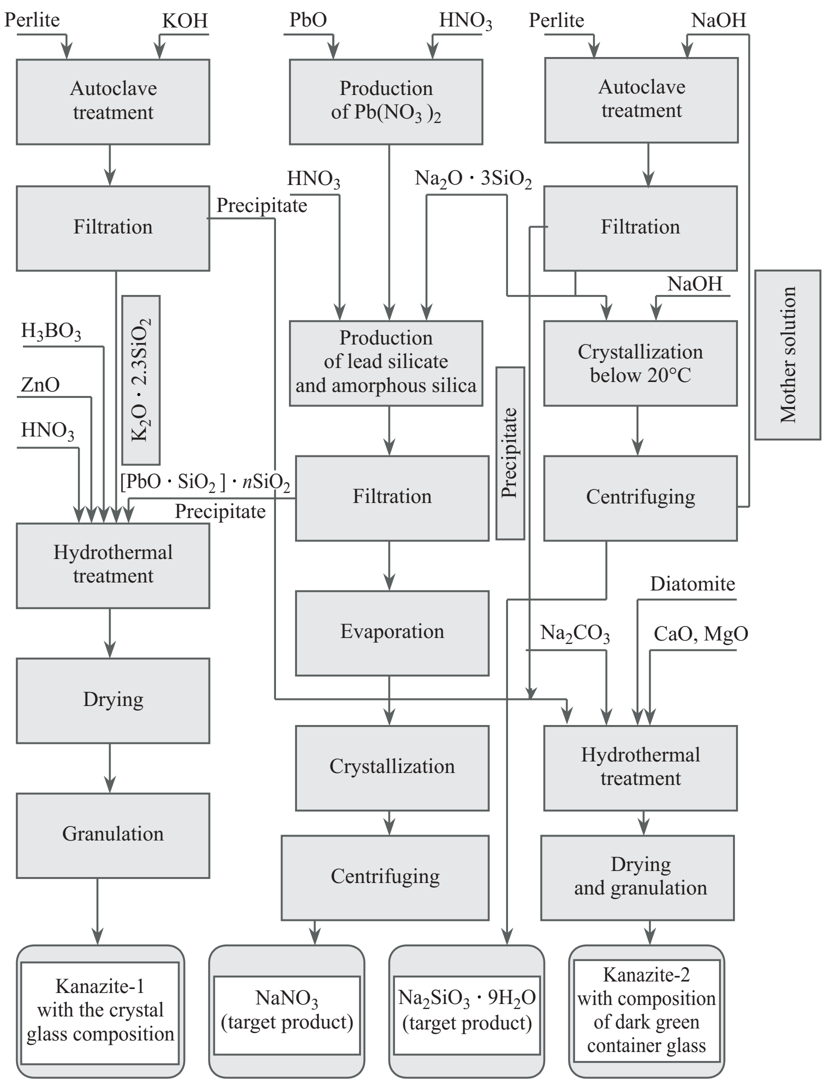

Fig. 1. Technological scheme of making kanazite-1 for crystal glass production.

reacts with liquid sodium glass, lead silicate with a high silicate modulus precipitates [8]. In this case it becomes unnecessary to increase the silicate modulus by carbonizing sodium liquid glass using carbon dioxide or to use nitric acid to neutralize the alkali, since the modulus is brought from 2.3 to 4.0 (to the prescribed modulus value) due to the high-modulus silicate additives. Introduction of lead oxide into kanazite in the form of lead silicate ensures the chemical homogeneity of the material and also substantially decreases the volatilization of lead oxide in crystal glass melting and simplifies the technology of producing kanazite-1 with the composition of potassium-lead crystal glass.

However, the production of lead nitrate in our country is limited. It has to be prepared on site using nitric acid and lead oxide.

An optimum regime for production of lead nitrated has been determined: milling of PbO to size 0.25 mm (100%), reaction temperature 70°C, nitric acid content 15 – 25%, treatment duration 5 – 10 min.

The reaction of lead nitrate production is

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

Potassium liquid glass, high-modulus lead silicate, and zinc oxide and boric acid in quantities calculated based on the prescribed glass composition are supplied in the synthesis of kanazite. Kanazite for production of crystal glass with a PbO content equal to 24% is produced from pure kanazite-forming components in a mixing tank at a temperature of 90 – 100°C under continuous mixing for 30 – 40 min [9]. After hydrothermal synthesis, the pulp is dried in a spray drier at 200 – 250°C, then kanazite of moisture 32 – 35% is sent to a screw granulator for granulation. The chemical processes occurring in the hydrothermal synthesis of kanazite with the crystal glass composition are indicated in Fig. 2.

Synthesis of kanazite-1 with the alkali-free composition by external addition of deficient silicate. The deficient quantity of silica is introduced into liquid glass in the form of amorphous silica. We developed a method for purification of diatomite with utilization of the waste acid. Mechanical impurities are removed from diatomite using the aqueous decanting method and then treated by 15% nitric acid (or hydrochloric acid for deep purification) in a jet reactor designed by V. G. Khachatryan. The diatomite suspension under a pressure of 0.32 – 0.35 MPa and a feed rate of 3.5 liters/sec is fed into a jet reactor with a nozzle diameter of 5 mm; the acid solution is vacuum-pumped from a dispenser via the lateral connecting pipe. After passing via the jet reactor, the suspension is filtered and the resulting precipitate is poured into liquid glass to ensure the required silicate modulus. The waste nitric acid reacts with milled lime or dolomite and produces solutions of calcium and magnesium nitrates used in the synthesis of kanazite-1. It is determined that the SiO_2 content in alkali aluminosilicate (AAL-2) can be brought up to 98%, and it can be introduced without drying into liquid glass to increase the silicate modulus [6].

Synthesis of kanazite-1 with the sheet glass composition. Finely milled silica-bearing rock (diatomite, tripolite, etc.) is treated in continuous autoclaves using a caustic soda solution of concentration 100 – 200 g/liter with the ratio of Na_2O in the solution to SiO_2 in the rock equal to 1.00 : 0.25 at temperatures of 150 – 200°C for 1 – 4 h. Depending on the rock type and the treatment conditions, the filtered solution of sodium silicate can have a silicate modulus from 1.0 to 3.8. Silicate solutions (liquid glasses) undergo deep purification from toxic colorant impurities (in particular, Fe_2O_3) by

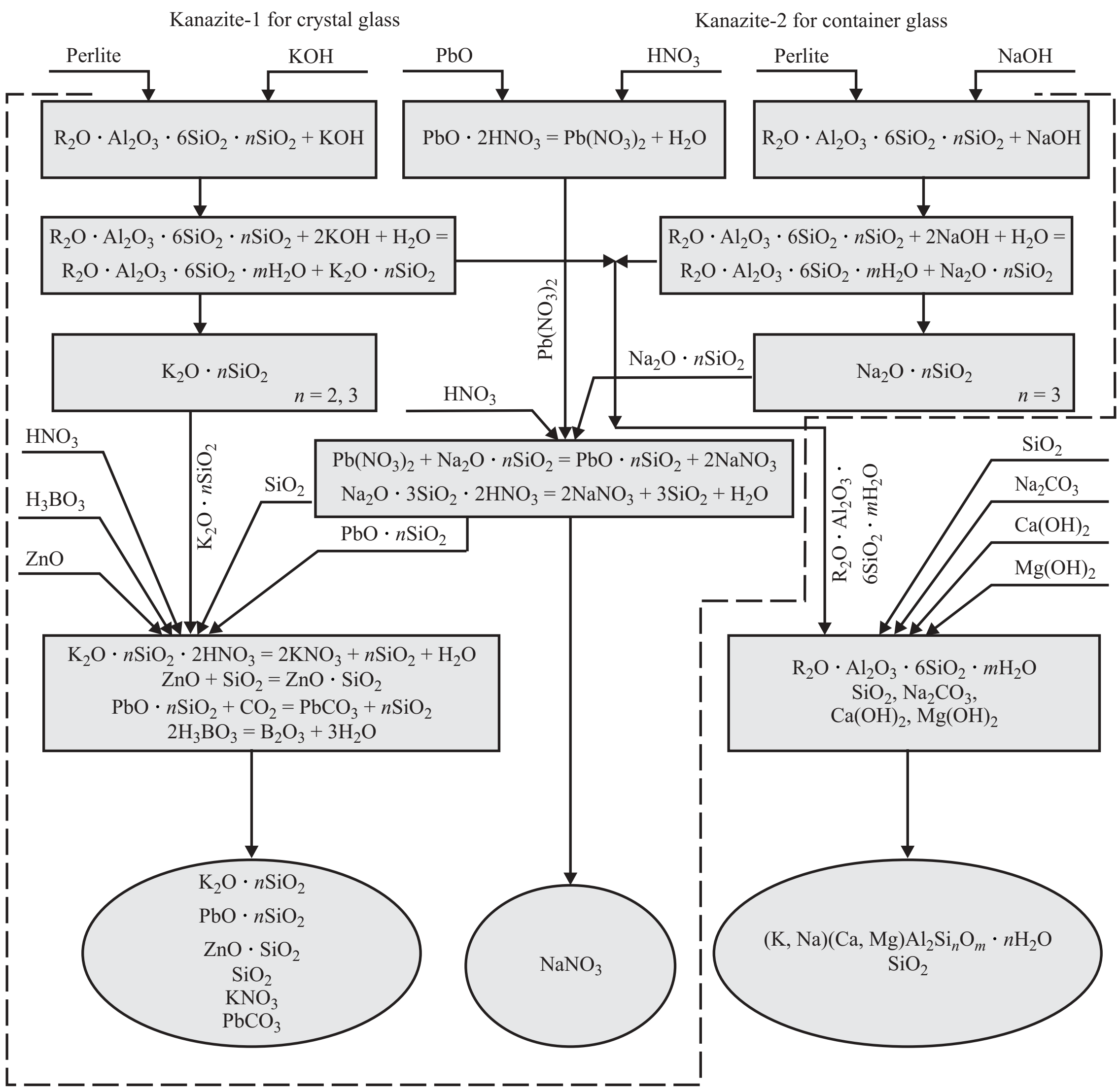

Fig. 2. Chemical processes in hydrothermal method of batch production for crystal glass.

the method developed by us involving a magnetic field. Clarified solutions are carbonized [10]:

$$Na_2O \cdot nSiO_2 + CO_2 + aq = Na_2CO_3 + nSiO_2 + aq.$$

After carbonizing, a part of the soda in the form of a solution is separated by filtration and the precipitate ($Na_2CO_3 \cdot nSiO_2$) without drying is used for the preparation of kanazite-1 for production of sheet glass with the following chemical composition (wt.%): 72.0 SiO_2, 1.5 Al_2O_3, 0.01 Fe_2O_3, 9.6 CaO, 3.0 MgO, and 14.0 Na_2O.

The soda solution is caustified by fired dolomite with regeneration of caustic soda:

$$2Na_2CO_3 + CaO \cdot MgO + 2H_2O = 4NaOH + CaCO_3 \cdot MgCO_3.$$

The pulp in this case is filtered. The caustic soda solution after evaporation is returned to the process and the precipitate (precipitated $CaCO_3 \cdot MgCO_3$) is used for the synthesis of kanazite with the sheet glass composition (Fig. 3). Depending on the prescribed glass composition, precipitates of $NaCO_3 \cdot nSiO_2$ and $CaCO_3 \cdot MgCO_3$ (moist) under constant stirring arrive at the mixing tank, then the pulp is pumped into a spray drier for drying and granulation.

Kanazite-1 with the sheet glass composition can be produced as well without fired dolomite (Fig. 3). First, calcium and magnesium carbonates are dissolved in 15 – 25% nitric acid (an exothermic reaction):

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2CO_3;$$

$$MgCO_3 + 2HNO_3 = Mg(NO_3)_2 + H_2CO_3.$$

The solution of calcium and magnesium nitrate undergoes deep purification from the colorant impurities by the addition of excess CaO, bringing the pH to 7, after which

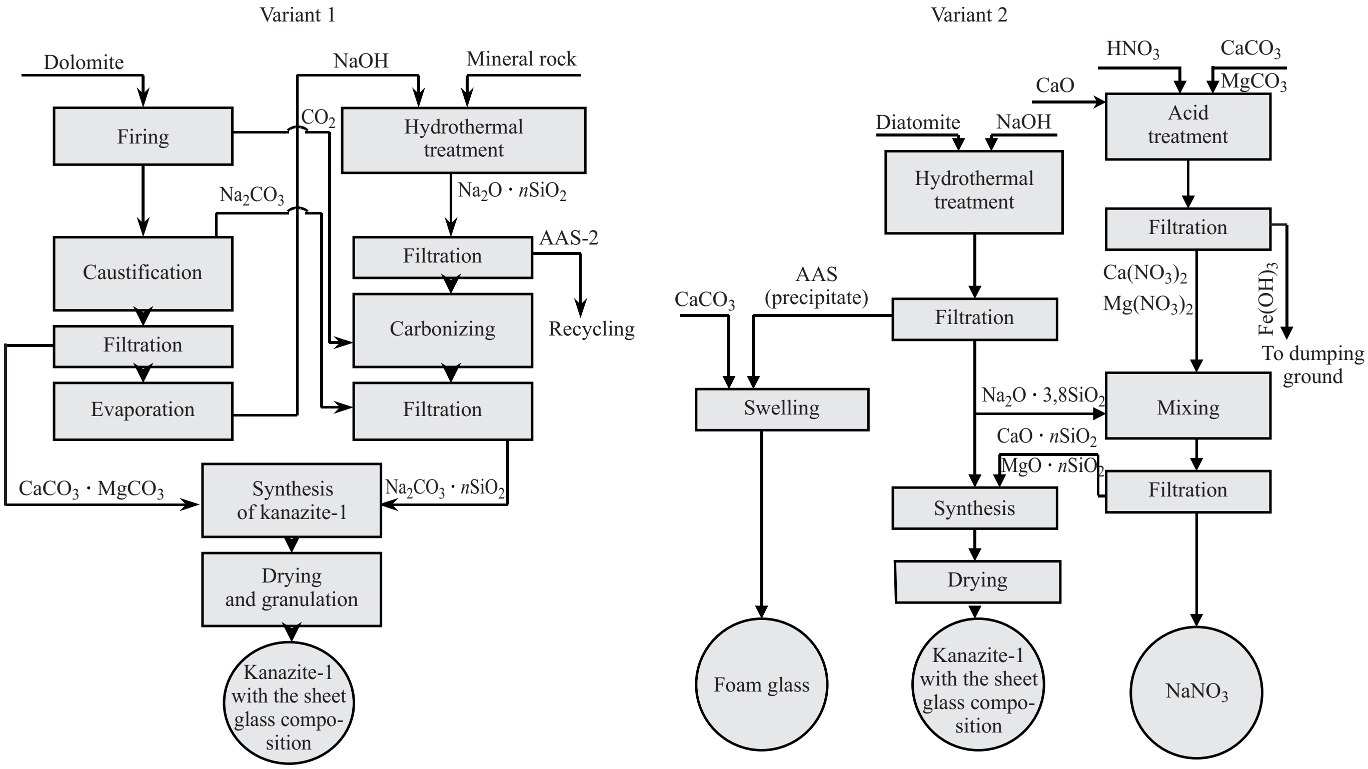

Fig. 3. Theoretical technological scheme for making kanazite with sheet-glass composition.

iron precipitates in the form of $Fe(OH)_3$ and is separated by filtration. The purified solutions of liquid glass, calcium nitrate, and magnesium nitrate react and produce calcium and magnesium silicates, which are separated by filtration:

$$Ca(NO_3)_2 + Na_2O \cdot nSiO_2 = CaO \cdot nSiO_2 + 2NaNO_3;$$

$$Mg(NO_3)_2 + Na_2O \cdot nSiO_2 = MgO \cdot nSiO_2 + 2NaNO_3.$$

Thus, the developed technology of complex processing of amorphous rocks makes it possible to involve new types of local materials in glass-melting, i.e., perlite, tripolite, diatomite, etc., which are not carcinogenic and whose reserves in our country are virtually unlimited.

Production of kanazite, which is a complex glass material, proceeds at the maximum rate of reactions, since the glass-forming components in the liquid phase react at the molecular level.

The method for glass production is developed omitting the liquid phase, i.e., the production of glass “from below” based on the hydrothermal treatment of amorphous rocks.

Owing to its specific amorphous phase composition and fine dispersion of the components, kanazite has a high reacting capacity intensifying the glass-melting processes, which makes it possible to decrease the glass-melting temperature by a few hundreds of degrees.

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